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27 January 2016

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Jin, Z. and West, A.J. and Zhang, F. and An, Z. and Hilton, R.G. and Yu, J. and Wang, J. and Li, G. and Deng, L. and Wang, X. (2016) 'Seismically enhanced solute fluxes in the Yangtze River headwaters following the A.D. 2008 Wenchuan earthquake.', *Geology*, 44 (1). pp. 47-50.

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Seismically enhanced solute fluxes in the Yangtze River headwaters following the 2008 Wenchuan earthquake

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ABSTRACT

Large earthquakes alter physical and chemical processes at the Earth's surface, triggering landslides, fracturing rock, changing large-scale permeability, and influencing hydrologic pathways. The resulting effects on global chemical cycles are not fully known. Here we show changes in the dissolved chemistry of the Min Jiang, in the Yangtze River headwaters, following the 2008 M_w 7.9 Wenchuan earthquake. Total solute fluxes transported by the Min Jiang increased after the earthquake, accompanied by a ~4x increase in Na*/Ca ratios (where Na* is Na⁺ corrected for atmospheric and evaporite contributions) and a 0.000644 ± 0.000146 increase in $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. These changes are consistent with enhanced contribution from silicate sources. We infer

that the CO₂ consumption rate via silicate-derived alkalinity increased 4.3 ± 0.4 times. If similar changes are associated with other large earthquakes, enhanced solute export could directly link tectonic activity with weathering and alkalinity fluxes that supply nutrients to ecosystems, influence seawater chemistry evolution, and steer Earth's long-term carbon cycle and climate.

INTRODUCTION

Rivers collect and transport material from across Earth's surface, so their chemistry integrates geological and environmental processes over space and time (e.g., Berner and Berner, 1996; Gaillardet et al., 1999). Variability in river chemistry over timescales from days to seasons to decades is increasingly well understood (e.g., Raymond and Cole, 2003; Tipper et al., 2006; Godsey et al., 2009; Torres et al., 2015), as are the global implications (Maher and Chamberlain, 2014). The effects of infrequent events such as large earthquakes on river chemistry are less well known, since these events are not typically represented in observational records even though their cumulative effects may be significant over the centennial or longer timescales of their recurrence.

Large earthquakes on continental faults perturb hydrologic pathways (Rojstaczer et al., 1995; Montgomery and Manga, 2003; Claesson et al., 2004; Skelton et al., 2014), and changes in solute chemistry of groundwaters and streams have been proposed as possible earthquake warning indicators (e.g. Rojstaczer et al., 1995; Skelton et al., 2014). Earthquake-driven changes in river solute fluxes could be important for quantifying (bio)geochemical fluxes and for understanding terrestrial geochemical and hydrological processes.

The chemical response of the Min Jiang in China to the 2008 M_w 7.9 Wenchuan earthquake provides a rare opportunity, allowing us to directly observe and quantify how a seismic event affects river chemical signatures. The Wenchuan opportunity arises in part because of data on Min Jiang river chemistry prior to 2008 (Qin et al., 2006; Yoon et al., 2008; Huh, 2010), providing the basis for direct comparison with samples collected after the earthquake.

The 2008 Wenchuan earthquake occurred along the Longmen Shan mountain range that forms the eastern margin of the Tibetan Plateau (Robert et al., 2010). The Longmen Shan is characterized by steep slopes and high relief, increasing in mean elevation by ~3500 m over less than 100 km distance (Fig. 1a). The geology of the region is dominated by bedrock with alumino-silicate minerals, including metamorphic argillaceous sandstone and flysch, granite and monzonitic granite, and detrital sediments, as well as limestones (Fig. DR1). The Wenchuan earthquake was generated along the Yingxiu–Beichuan and Pengguan faults that run S40–50°NE along the Longmen Shan (Xu et al., 2009). The earthquake and associated aftershocks caused more than 56,000 landslides over ~200 km length of the mountain range, whereas the extent of landslides in the region was limited prior to the earthquake (Li et al., 2014). The climate of the region is dominated by the Asian and Indian summer monsoons, with 75% of annual precipitation (600–1100 mm/yr) during May to October. The annual water discharge of the Min Jiang, the major river draining the Longmen Shan, was $1.06 \times 10^{10} \text{ m}^3$ in 2000–2011, and the difference of annual water discharge before and after the earthquake was < 20% (Fig. 2a), smaller than inter-annual variability (Wang et al., 2015).

MATERIALS AND METHODS

River water samples for this study were collected weekly between December 2009 and the end of 2011 from two hydrological stations, at Weizhou and Zhenjiangguan, both on the main course of the Min Jiang (Fig. 1). Hydrologic parameters at both stations are monitored regularly by the Chinese Hydrology Bureau (CHB). The Weizhou station in the town of Wenchuan lies in the zone of high peak ground acceleration (PGA) during the 2008 earthquake, and consequently in a region significantly affected by co-seismic landslides and other visible damage (Fig. 1). The Zhenjiangguan station is farther upstream, still within the zone of measurable earthquake-associated ground acceleration, but where PGA was much lower than at Weizhou and where there were few earthquake-triggered landslides (Fig. 1). In addition, single samples were collected in 2011 from nine revisited sites distributed throughout the river basin (Fig. 1), matching sites that had been sampled at least once before the earthquake (Qin et al., 2006; Yoon et al., 2008; Huh, 2010). Filtered water samples were analyzed for dissolved major ions and Sr^{2+} concentrations, and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (Table DR1, Figs. DR2-4; see Methods in the GSA Data Repository). The chemistry of the samples collected in this study was compared to dissolved chemistry data from prior to the earthquake at equivalent sites. The data set from the Weizhou station enables comparison of pre- and post-earthquake annual time-series (Table DR2). For the other samples, collection season was matched as closely as possible to previous studies (Table DR3).

RESULTS

Pre- and Post-Earthquake Times-Series from Weizhou Station

When comparing data at Weizhou from 2010–2011 versus data from 2001–2002, prior to the earthquake, a systematic increase is observed in Na^*/Ca molar ratios (Fig. 2b, where $\text{Na}^* = \text{Na}^+$ derived from silicate weathering; see Methods in the GSA Data Repository) and K/Ca ratios (Fig. DR5). These differences are significantly greater than the variability observed in the long-term record of dissolved chemistry for the Min Jiang acquired by the CHB between the 1970s and 2000 (Qin et al., 2006), suggesting that the higher ratios observed in the 2010–2011 data reflect a distinct post-earthquake change in solute composition. Unlike concentrations, elemental and isotopic ratios are not directly influenced by dilution, so the observed changes cannot be explained by changes in precipitation or discharge amounts. The changes in elemental ratios are also accompanied by an increase in the average dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from 0.712663 ± 0.000200 to 0.713307 ± 0.000207 . Coincident increases in dissolved Na^* , K^+ , and $^{87}\text{Sr}/^{86}\text{Sr}$ are consistent with silicate mineral sources. Ratios of Mg/Ca and Sr/Ca do not show similar changes (Fig. DR3), most likely because river waters are at carbonate saturation both before and after the earthquake (Yoon et al., 2008).

Paired Data from Other Sites

Pre-earthquake time series data are not available at Zhenjiangguan (cf. Fig. DR6), but we can compare individual paired data from before and after the earthquake at this site and several others. Increases in both Na^*/Ca and Sr isotope ratios (Figs. 1b, c and 3a, b) are observed at all of the sites within the zone of significant PGA, and the direction of change is consistent with that observed at Weizhou (Fig. 2). The magnitude of post-earthquake Na^*/Ca increase (0.02 – 0.22 , mean 0.07 ± 0.07) at these paired sites is significantly larger than the annual variability at Weizhou (0.02 , 1σ pre-earthquake; 0.04 ,

1 σ post-earthquake) and Zhenjiangguan (0.03, 1 σ post-earthquake), suggesting that the observed changes are not artifacts of the times of sample collection. Sites 1 and 2, farthest from the Wenchuan earthquake epicenter and activated faults, show relatively little change in Na*/Ca after the earthquake (less than 0.02), reflecting their greater distance from the region of strongest PGA (Fig. 3).

The relationship between the magnitude of observed change (Δ , difference between post- and pre-earthquake ratios) in solute chemistry and mean PGA during the Wenchuan earthquake in the catchment area upstream of each sampling site is not straightforward (Fig. 3c, d). Nonetheless, for the main stem, sites showing highest Δ values for both Na*/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ are ones where mean PGA was relatively high (e.g., sites 7 and 8, and at Weizhou), while sites with lower PGA are associated with least chemical change (e.g., site 2). For the tributary sites, the relationship is less clear, with sites 3, 4 and 5 all showing large changes in Na*/Ca despite a range in catchment-averaged PGA (Figs. 1b, 3c). The larger magnitude of $\Delta\text{Na}^*/\text{Ca}$ at tributary sites compared to the main stem and the lack of relationship to PGA might be explained by smaller tributary catchment areas, such that smaller perturbations have a greater effect than on the main stem. Overall, the first-order relationship with PGA for the main stem (i.e., significant change within the earthquake-affected zone, but less change farther from the center of this zone at sites 1 and 2) is consistent with a link between the earthquake and observed changes in river chemistry.

DISCUSSION

Causes of Changing River Chemistry Following the Wenchuan Earthquake

135 The dissolved Na^*/Ca , K/Ca , and $^{87}\text{Sr}/^{86}\text{Sr}$ of the Min Jiang systematically shifted
136 towards more silicate compositions across multiple sites and over multiple years
137 following the Wenchuan earthquake. Observed changes persisted at least for 3 years
138 (through December of 2011, when the last samples in this study were collected), so any
139 perturbation must have responded rapidly and been sustained for several years. Release
140 of deep basinal brines or greater contribution from human activities are unlikely causes
141 since we do not observe coincident changes in Cl^- or SO_4^{2-} concentrations, as would be
142 expected for such sources (e.g., Gaillardet et al., 1999). Herein we propose that the
143 observed changes are related to the effects of earthquake shaking on fluid pathways and
144 the minerals exposed to fluids by bedrock fracturing and/or by seismic landslides.

145 In more detail, at shallow depths (centimeters to several meters depth),
146 earthquakes trigger extensive co- and post-seismic landslides (e.g., Li et al., 2014), which
147 can act as solute generators by producing reactive fine-grained sediment (Wang et al.,
148 2015) and by focusing flow through this material (e.g., Watanabe et al., 2005; Emberson
149 et al., in press). Leaching of exchangeable cations from finely ground landslide debris
150 could also contribute to the solute load. Co-seismic landslides are prevalent throughout
151 the lower reaches of the Min Jiang study region (Li et al., 2014; Fig. 1), but the spatial
152 extent of observed changes in solute chemistry extends beyond the zone of most
153 concentrated mapped landslide activity, suggesting that other processes play a major role.

154 At greater depths of tens to hundreds of meters, earthquakes can fracture rock
155 (Molnar et al., 2007), alter permeability (Rojstaczer et al., 1995), and perturb hydrologic
156 systems over regional to continental scales, extending beyond regions of visible co-
157 seismic damage (Montgomery and Manga, 2003; Skelton et al., 2014; Shi et al., 2015).

Direct measurements of permeability along the Pengguan and Beichuan fault zones showed initial increase followed by healing over exponential decay times of 0.6–2.5 years (Xue et al., 2013), but larger spatial scale changes in the hydrologic system following shaking and seismic disturbance may persist for longer (Rojstaczer et al., 1995; Claesson et al., 2004; Skelton et al., 2014). Groundwaters are typically concentrated in silicate-derived cations as a result of prolonged water-rock contact (e.g., Tipper et al., 2006). Post-seismic discharge of such groundwater could shift river chemistry toward higher solute fluxes and more silicate composition. Evacuation of waters close to equilibrium and replacement with more dilute waters could also stimulate higher mineral dissolution rates (Maher and Chamberlain, 2014; Rempe and Dietrich, 2014), as could the exposure of new mineral surfaces (White and Brantley, 2003), for example in bedrock micro-fractures.

With the current data, we are not able to distinguish definitively the contribution from seismically altered flowpaths versus enhanced dissolution in landslide debris, nor can we distinguish whether additional solutes have their immediate source from primary minerals, exchangeable sites, or concentrated groundwaters. Greater mechanistic insight might be gained by future studies tracking spatial patterns of hydrochemical change and longer-term evolution, including the return to pre-earthquake river composition.

Implications for Geochemical Fluxes

Independent of mechanism, the results from the Min Jiang offer empirical evidence that a high-magnitude, low-frequency earthquake can have a significant, previously-unrecognized effect on river chemistry. The increased flux of alkalinity following the Wenchuan earthquake enhanced CO₂ drawdown and contributed more

radiogenic ^{87}Sr to the oceans. The post-earthquake dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Min Jiang main stem river waters increased by a mean of 0.000644 ± 0.000146 relative to those prior to the earthquake (excluding site 2). Sr concentrations did not significantly change at the same time (Figs. DR3 and 4), implying a net increase in the delivery of ^{87}Sr to the oceans, with potential implications for interpreting the geologic record of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ composition (Raymo et al., 1988; Edmond, 1992). The rates of net CO_2 consumption associated with silicate alkalinity (OCO_2) after the earthquake (2010–2011) are 4.3 ± 0.4 times higher than prior to the earthquake, based on average monthly solute concentrations, drainage area, and water discharge (see Methods in the GSA Data Repository). Assumptions about the composition of the silicate mineral end-member do not affect the relative magnitude of OCO_2 before and after the earthquake, as long as the composition of silicate minerals did not change significantly.

The Wenchuan case suggests that changes in tectonic activity have the potential to increase riverine alkalinity fluxes to the oceans by changing the frequency of earthquakes. The extent to which such seismic changes in solute flux affect seawater composition and the global carbon cycle (e.g., Raymo et al., 1988; Berner, 2004) remains to be assessed. The magnitude of long-term change will depend on the duration that earthquake-triggered changes persist and how the extent of chemical change varies for different earthquakes. Whether other earthquakes cause similar effects may relate to a number of factors including event magnitude, regional seismicity and earthquake return times, the extent of induced landslides, the nature of fracture development and changes in hydrological pathways, and regional lithology. These questions will only be answered by further investigation to explore how the magnitude and duration of change vary for

different earthquakes, and to understand the underlying mechanisms causing observed changes.

ACKNOWLEDGMENTS

This work was funded by 973 Program (2013CB956402) and NSFC grants to Z.J.; CAS YIS Fellowships to A.J.W. and R.G.H.; and U.S. NSF grant EAR 1053504 to A.J.W. We thank M. He, Y. Zhu, Y. Liu and C. Zhang for help for sample collection and measurements. The research benefited from discussions with M.E. Raymo, G.J. Li and J. Gaillardet. P. Chamberlain, S. Brantley and S. Anderson are thanked for their insightful comments that improved the manuscript in review.

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FIGURE CAPTIONS

Figure 1. (a) Map of the 2008 M_w 7.9 Wenchuan earthquake region, showing sampling
sites, epicenter, co-seismic landslides (yellow polygons, from Li et al., 2014), and
contours for peak ground accelerations (PGA, from USGS earthquake hazard program,
<http://earthquake.usgs.gov/earthquakes>). Dots with stars inside are river water sample
sites at Weizhou and Zhenjianguan hydrological stations; dots (main stem) and
diamonds (tributaries) are revisited sites along the Min Jiang (1, Source of the Min Jiang;
2, Songpan; 3, Riwu Qu; 4, Heishui; 5, Zagunao; 6, Wenchuan; 7, Yingxiu; 8, Guan
Xian; 9, Dujiangyan). The magnitudes of observed change (Δ) in (b) Na^*/Ca and (c)
 $^{87}\text{Sr}/^{86}\text{Sr}$ are shown by color shading.

Figure 2. (a) Seasonal patterns of Min Jiang river water discharge before and after the 2008 Wenchuan earthquake. Water discharge totaled $11.5 \times 10^9 \text{ m}^3$ (2005) and $11.9 \times 10^9 \text{ m}^3$ (2010) at the Weizhou station. (b) Annual time series of Na^*/Ca ratios, with means and standard deviations (1σ) on the right of the panel; pre-earthquake (EQ) data are from samples collected near the Weizhou station in 2001 and 2002 (Qin et al., 2006).

Figure 3. Comparison of Min Jiang river dissolved (a) Na^*/Ca and (b) $^{87}\text{Sr}/^{86}\text{Sr}$ before and after the 2008 Wenchuan earthquake. Data are for water samples collected from the same sites and during the same seasons. Pre-EQ data are from Qin et al. (2006), Yoon et al. (2008) and Huh (2010); post-EQ data are from the samples collected in 2011 in this study. Pre-EQ $^{87}\text{Sr}/^{86}\text{Sr}$ data are not available for tributary sites. Analytical uncertainties are smaller than symbol sizes. Gray shading in (a) shows the pre-EQ Na^*/Ca variability of 0.02 (1σ). The site numbers correspond to Figure 1; ZJG and WZ are Zhenjiangguan and Weizhou stations, respectively. Magnitude of changes (Δ) between pre-EQ and post-EQ can be compared to the mean PGA in each catchment (c and d). Bars for WZ in (c) show standard deviations (1σ) of the data in Figure 2b.

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